

## 2,6,6-Trimethylcyclohexene-1-carbaldehyde oxime

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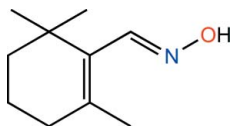
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.053;  $wR$  factor = 0.191; data-to-parameter ratio = 28.3.

In the crystal of the title compound  $\text{C}_{10}\text{H}_{17}\text{NO}$ , synthesized by the reaction of  $\beta$ -cyclocitral with hydroxylamine hydrochloride, inversion-related molecules are linked by a pair of  $\text{O}-\text{H}\cdots\text{N}$  hydrogen-bonding interactions between the oxime functionalities, forming  $R_2^2(6)$  loops. The molecular conformation is stabilized by intramolecular methyl  $\text{C}-\text{H}\cdots\text{N}$  interactions. The cyclohexene ring has the typical half-chair conformation.

### Related literature

For applications of oximes in organic syntheses, see: Cerny *et al.* (1969); Donaruma & Heldt (1960); Kutney *et al.* (1992); Touster (1953). For graph-set notation, see: Etter *et al.* (1990); Bernstein *et al.* (1995).



### Experimental

#### Crystal data

$\text{C}_{10}\text{H}_{17}\text{NO}$   
 $M_r = 167.25$   
 Triclinic,  $P\bar{1}$   
 $a = 7.5670$  (3) Å

$b = 7.7208$  (3) Å  
 $c = 9.3072$  (4) Å  
 $\alpha = 81.212$  (3)°  
 $\beta = 76.590$  (3)°

$\gamma = 71.385$  (3)°  
 $V = 499.43$  (4) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation

$\mu = 0.07$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.09 \times 0.06 \times 0.05$  mm

#### Data collection

Bruker SMART APEXII CCD  
 area-detector diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2008)  
 $T_{\min} = 0.994$ ,  $T_{\max} = 0.997$

13971 measured reflections  
 3341 independent reflections  
 2134 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.191$   
 $S = 1.06$   
 3341 reflections  
 118 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.14$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                           | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| $\text{O1}-\text{H1}\cdots\text{N1}^i$  | 0.86 (3) | 2.02 (3)    | 2.8346 (18) | 158 (2)       |
| $\text{C9}-\text{H9A}\cdots\text{N1}$   | 0.96     | 2.57        | 3.1979 (19) | 123           |
| $\text{C10}-\text{H10A}\cdots\text{N1}$ | 0.96     | 2.43        | 3.0762 (17) | 125           |

Symmetry code: (i)  $-x + 1, -y, -z + 1$ .

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

PTM and SJJ thank the DST India (FIST programme) for the use of the diffractometer at the School of Chemistry, Bharathidasan University, Tiruchirappalli, Tamilnadu, India.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2144).

### References

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**supplementary materials**

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## 2,6,6-Trimethylcyclohexene-1-carbaldehyde oxime

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### Comment

An oxime is an important functional group in organic chemistry because it is not only used as an efficient protecting group for carbonyls but also may be used for the purification of carbonyl compounds (Donaruma & Heldt, 1960). Moreover oximes are used for the preparation of many compounds such as amines by reduction (Cerny *et al.*, 1969), nitro compounds by oxidation, amides by the Beckmann rearrangement and carbonyl compounds from non carbonyl compounds (Touster, 1953). The title compound  $C_{10}H_{17}NO$  is a key intermediate in the synthesis of aroma compounds such as  $\beta$ -cyclogeranyl nitrile which can be used for the synthesis of the important aroma compound  $\beta$ -damascone (Kutney *et al.*, 1992). Herein, we report the crystal structure of the title compound (Fig. 1) in which each molecule is connected to an inversion-related molecule through  $O-H\cdots N$  hydrogen bonds, (Table 1) forming a cyclic dimer [graph-set  $R^2_2(6)$  (Etter *et al.*, 1990; Bernstein *et al.*, 1995)] (Fig. 2). These cyclic DA—AD (Donor Acceptor—Acceptor Donor) interactions involving pairs of  $O-H\cdots N$  hydrogen bonds between the oxime functionalities are similar to the  $O-H\cdots O$  interactions observed in carboxylic acid dimers. The crystal structure is stabilized by intramolecular methyl  $C-H\cdots N_{oxime}$  hydrogen-bonding interactions.

### Experimental

To a mixture of 4.6 g (0.065 mol) of hydroxylamine hydrochloride in 50 ml of  $H_2O$  and 10 g (0.065 mol) of  $\beta$ -cyclocitral, a solution of 3.5 g (0.033 mol) of sodium carbonate in 15 ml of  $H_2O$  was added dropwise. The mixture was stirred at room temperature for ten minutes and the solid product which formed was collected and recrystallized from hexane.

### Refinement

The H atoms attached to C7 and O1 were located from a difference Fourier map and were refined freely. The remaining H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with  $U_{iso}(H)$  set at  $1.2U_{eq}(C)$  except for the methyl hydrogen atoms which were refined with  $U_{iso}(H)$  set at  $1.5U_{eq}(C)$ .

### Figures

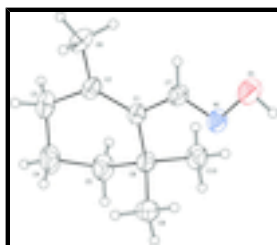


Fig. 1. The molecular structure of the title compound, with atom labels and anisotropic displacement ellipsoids drawn at the 50% probability level.

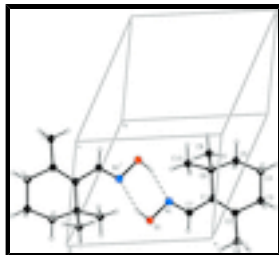


Fig. 2. The centrosymmetric  $R^2_2(6)$  hydrogen-bonded dimer units, with hydrogen bonds shown as dashed lines. For symmetry code (i), see Table 1.

## 2,6,6-Trimethylcyclohexene-1-carbaldehyde oxime

### Crystal data

|                                |   |
|--------------------------------|---|
| $C_{10}H_{17}NO$               | $Z = 2$   |
| $M_r = 167.25$                 | $F(000) = 184$  |
| Triclinic, $P\bar{1}$          | $D_x = 1.112 \text{ Mg m}^{-3}$                         |
| Hall symbol: $-P\ 1$           | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $a = 7.5670 (3) \text{ \AA}$   | Cell parameters from 3341 reflections                   |
| $b = 7.7208 (3) \text{ \AA}$   | $\theta = 2.3\text{--}33.0^\circ$                       |
| $c = 9.3072 (4) \text{ \AA}$   | $\mu = 0.07 \text{ mm}^{-1}$                            |
| $\alpha = 81.212 (3)^\circ$    | $T = 296 \text{ K}$                                     |
| $\beta = 76.590 (3)^\circ$     | Prism, colourless                                       |
| $\gamma = 71.385 (3)^\circ$    | $0.09 \times 0.06 \times 0.05 \text{ mm}$               |
| $V = 499.43 (4) \text{ \AA}^3$ |   |

### Data collection

|  |  |
|--|--|
| Bruker SMART APEXII CCD area-detector diffractometer     | 3341 independent reflections   |
| Radiation source: fine-focus sealed tube graphite        | 2134 reflections with $I > 2\sigma(I)$                                 |
| $\varphi$ and $\omega$ scans                             | $R_{\text{int}} = 0.022$   |
| Absorption correction: multi-scan (SADABS; Bruker, 2008) | $\theta_{\text{max}} = 33.0^\circ$ , $\theta_{\text{min}} = 2.3^\circ$ |
| $T_{\text{min}} = 0.994$ , $T_{\text{max}} = 0.997$      | $h = -11 \rightarrow 11$   |
| 13971 measured reflections                               | $k = -11 \rightarrow 11$   |
|  | $l = -12 \rightarrow 13$   |

### Refinement

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | Primary atom site location: structure-invariant direct methods         |
| Least-squares matrix: full      | Secondary atom site location: difference Fourier map                   |
| $R[F^2 > 2\sigma(F^2)] = 0.053$ | Hydrogen site location: inferred from neighbouring sites               |
| $wR(F^2) = 0.191$               | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.06$                      | $w = 1/[\sigma^2(F_o^2) + (0.0999P)^2 + 0.036P]$                       |
| 3341 reflections                | where $P = (F_o^2 + 2F_c^2)/3$   |
|                                 | $(\Delta/\sigma)_{\text{max}} < 0.001$                                 |

118 parameters

$$\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.14 \text{ e } \text{\AA}^{-3}$$

### Special details

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement.** Refinement on  $F^2$  for ALL reflections except those flagged by the user for potential systematic errors. Weighted  $R$ -factors  $wR$  and all goodnesses of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The observed criterion of  $F^2 > \sigma(F^2)$  is used only for calculating  $-R$ -factor-obs *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|      | <i>x</i>     | <i>y</i>      | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|---------------|--------------|----------------------------------|
| O1   | 0.60371 (16) | -0.14350 (15) | 0.37650 (16) | 0.0794 (5)                       |
| N1   | 0.67895 (14) | 0.00174 (14)  | 0.37695 (13) | 0.0552 (4)                       |
| C1   | 0.94463 (15) | 0.11492 (15)  | 0.25083 (13) | 0.0425 (3)                       |
| C2   | 1.12581 (16) | 0.05523 (17)  | 0.17581 (14) | 0.0492 (3)                       |
| C3   | 1.26022 (18) | 0.1703 (2)    | 0.1444 (2)   | 0.0680 (5)                       |
| C4   | 1.1923 (2)   | 0.3358 (2)    | 0.2335 (2)   | 0.0772 (6)                       |
| C5   | 0.9848 (2)   | 0.42925 (19)  | 0.2342 (2)   | 0.0656 (5)                       |
| C6   | 0.85762 (15) | 0.30698 (15)  | 0.30624 (14) | 0.0458 (3)                       |
| C7   | 0.83019 (17) | -0.01188 (16) | 0.27932 (16) | 0.0505 (4)                       |
| C8   | 1.2169 (2)   | -0.1322 (2)   | 0.11773 (18) | 0.0689 (5)                       |
| C9   | 0.8338 (2)   | 0.2967 (2)    | 0.47500 (17) | 0.0641 (5)                       |
| C10  | 0.66297 (19) | 0.40088 (18)  | 0.26268 (19) | 0.0627 (5)                       |
| H1   | 0.509 (3)    | -0.126 (3)    | 0.450 (3)    | 0.107 (7)*                       |
| H3A  | 1.27880      | 0.21180       | 0.03980      | 0.0820*                          |
| H3B  | 1.38250      | 0.09430       | 0.16530      | 0.0820*                          |
| H4A  | 1.21150      | 0.29760       | 0.33440      | 0.0930*                          |
| H4B  | 1.26500      | 0.42070       | 0.19030      | 0.0930*                          |
| H5A  | 0.96760      | 0.46760       | 0.13290      | 0.0790*                          |
| H5B  | 0.94450      | 0.53850       | 0.28720      | 0.0790*                          |
| H7   | 0.866 (2)    | -0.116 (2)    | 0.2260 (19)  | 0.074 (5)*                       |
| H8A  | 1.29070      | -0.21220      | 0.18590      | 0.1030*                          |
| H8B  | 1.29810      | -0.12140      | 0.02290      | 0.1030*                          |
| H8C  | 1.11960      | -0.18180      | 0.10750      | 0.1030*                          |
| H9A  | 0.75450      | 0.22010       | 0.52080      | 0.0960*                          |
| H9B  | 0.77580      | 0.41760       | 0.50780      | 0.0960*                          |
| H9C  | 0.95610      | 0.24580       | 0.50220      | 0.0960*                          |
| H10A | 0.57850      | 0.32850       | 0.30550      | 0.0940*                          |
| H10B | 0.67810      | 0.41230       | 0.15670      | 0.0940*                          |
| H10C | 0.61080      | 0.52050       | 0.29870      | 0.0940*                          |

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$   | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|------------|-------------|-------------|-------------|-------------|-------------|
| O1  | 0.0698 (7) | 0.0627 (6)  | 0.1080 (10) | -0.0392 (5) | 0.0201 (6)  | -0.0293 (6) |
| N1  | 0.0466 (5) | 0.0490 (5)  | 0.0702 (8)  | -0.0218 (4) | 0.0031 (5)  | -0.0113 (5) |
| C1  | 0.0377 (5) | 0.0448 (5)  | 0.0424 (6)  | -0.0118 (4) | -0.0047 (4) | -0.0018 (4) |
| C2  | 0.0404 (5) | 0.0555 (6)  | 0.0453 (7)  | -0.0109 (5) | -0.0021 (5) | -0.0023 (5) |
| C3  | 0.0404 (6) | 0.0793 (9)  | 0.0796 (11) | -0.0225 (6) | 0.0014 (6)  | -0.0022 (8) |
| C4  | 0.0539 (8) | 0.0782 (10) | 0.1078 (14) | -0.0362 (7) | -0.0069 (8) | -0.0105 (9) |
| C5  | 0.0586 (8) | 0.0526 (7)  | 0.0853 (11) | -0.0243 (6) | -0.0051 (7) | -0.0019 (7) |
| C6  | 0.0399 (5) | 0.0433 (5)  | 0.0530 (7)  | -0.0131 (4) | -0.0055 (5) | -0.0046 (5) |
| C7  | 0.0459 (6) | 0.0439 (6)  | 0.0588 (8)  | -0.0136 (4) | 0.0000 (5)  | -0.0105 (5) |
| C8  | 0.0548 (7) | 0.0692 (9)  | 0.0673 (10) | -0.0053 (6) | 0.0068 (7)  | -0.0172 (7) |
| C9  | 0.0694 (8) | 0.0688 (8)  | 0.0574 (8)  | -0.0237 (7) | -0.0063 (7) | -0.0171 (7) |
| C10 | 0.0491 (7) | 0.0496 (7)  | 0.0859 (11) | -0.0041 (5) | -0.0184 (7) | -0.0100 (6) |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|           |             |            |            |
|-----------|-------------|------------|------------|
| O1—N1     | 1.4113 (16) | C4—H4A     | 0.9700     |
| O1—H1     | 0.86 (3)    | C4—H4B     | 0.9700     |
| N1—C7     | 1.2714 (18) | C5—H5A     | 0.9700     |
| C1—C6     | 1.5334 (16) | C5—H5B     | 0.9700     |
| C1—C7     | 1.4608 (18) | C7—H7      | 0.942 (15) |
| C1—C2     | 1.3530 (18) | C8—H8A     | 0.9600     |
| C2—C8     | 1.5136 (19) | C8—H8B     | 0.9600     |
| C2—C3     | 1.506 (2)   | C8—H8C     | 0.9600     |
| C3—C4     | 1.514 (2)   | C9—H9A     | 0.9600     |
| C4—C5     | 1.503 (2)   | C9—H9B     | 0.9600     |
| C5—C6     | 1.534 (2)   | C9—H9C     | 0.9600     |
| C6—C9     | 1.532 (2)   | C10—H10A   | 0.9600     |
| C6—C10    | 1.538 (2)   | C10—H10B   | 0.9600     |
| C3—H3A    | 0.9700      | C10—H10C   | 0.9600     |
| C3—H3B    | 0.9700      |            |            |
| N1—O1—H1  | 103.3 (15)  | H4A—C4—H4B | 108.00     |
| O1—N1—C7  | 111.09 (11) | C4—C5—H5A  | 109.00     |
| C2—C1—C6  | 122.81 (11) | C4—C5—H5B  | 109.00     |
| C6—C1—C7  | 119.71 (10) | C6—C5—H5A  | 109.00     |
| C2—C1—C7  | 117.48 (11) | C6—C5—H5B  | 109.00     |
| C1—C2—C8  | 124.63 (12) | H5A—C5—H5B | 108.00     |
| C3—C2—C8  | 112.81 (12) | N1—C7—H7   | 113.3 (10) |
| C1—C2—C3  | 122.55 (12) | C1—C7—H7   | 121.4 (10) |
| C2—C3—C4  | 113.94 (13) | C2—C8—H8A  | 109.00     |
| C3—C4—C5  | 109.66 (13) | C2—C8—H8B  | 109.00     |
| C4—C5—C6  | 113.33 (12) | C2—C8—H8C  | 109.00     |
| C1—C6—C9  | 110.71 (10) | H8A—C8—H8B | 109.00     |
| C1—C6—C10 | 110.80 (10) | H8A—C8—H8C | 109.00     |
| C5—C6—C9  | 109.05 (12) | H8B—C8—H8C | 109.00     |

|              |              |               |              |
|--------------|--------------|---------------|--------------|
| C5—C6—C10    | 106.66 (11)  | C6—C9—H9A     | 109.00       |
| C9—C6—C10    | 109.18 (11)  | C6—C9—H9B     | 109.00       |
| C1—C6—C5     | 110.33 (10)  | C6—C9—H9C     | 109.00       |
| N1—C7—C1     | 125.29 (12)  | H9A—C9—H9B    | 109.00       |
| C2—C3—H3A    | 109.00       | H9A—C9—H9C    | 109.00       |
| C2—C3—H3B    | 109.00       | H9B—C9—H9C    | 110.00       |
| C4—C3—H3A    | 109.00       | C6—C10—H10A   | 109.00       |
| C4—C3—H3B    | 109.00       | C6—C10—H10B   | 109.00       |
| H3A—C3—H3B   | 108.00       | C6—C10—H10C   | 109.00       |
| C3—C4—H4A    | 110.00       | H10A—C10—H10B | 110.00       |
| C3—C4—H4B    | 110.00       | H10A—C10—H10C | 109.00       |
| C5—C4—H4A    | 110.00       | H10B—C10—H10C | 109.00       |
| C5—C4—H4B    | 110.00       |               |              |
| O1—N1—C7—C1  | -179.61 (12) | C7—C1—C6—C10  | -49.10 (16)  |
| C6—C1—C2—C3  | 2.0 (2)      | C2—C1—C7—N1   | 161.31 (13)  |
| C6—C1—C2—C8  | -179.34 (12) | C6—C1—C7—N1   | -18.5 (2)    |
| C7—C1—C2—C3  | -177.72 (13) | C1—C2—C3—C4   | 13.8 (2)     |
| C7—C1—C2—C8  | 0.89 (19)    | C8—C2—C3—C4   | -165.00 (13) |
| C2—C1—C6—C5  | 13.24 (17)   | C2—C3—C4—C5   | -44.02 (19)  |
| C2—C1—C6—C9  | -107.58 (14) | C3—C4—C5—C6   | 61.57 (18)   |
| C2—C1—C6—C10 | 131.13 (13)  | C4—C5—C6—C1   | -45.18 (17)  |
| C7—C1—C6—C5  | -167.00 (12) | C4—C5—C6—C9   | 76.62 (16)   |
| C7—C1—C6—C9  | 72.19 (15)   | C4—C5—C6—C10  | -165.59 (13) |

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

| <i>D</i> —H $\cdots$ <i>A</i>  | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1—H1 $\cdots$ N1 <sup>i</sup> | 0.86 (3)    | 2.02 (3)            | 2.8346 (18)                | 158 (2)                       |
| C9—H9A $\cdots$ N1             | 0.96        | 2.57                | 3.1979 (19)                | 123                           |
| C10—H10A $\cdots$ N1           | 0.96        | 2.43                | 3.0762 (17)                | 125                           |

Symmetry codes: (i)  $-x+1, -y, -z+1$ .

Fig. 1

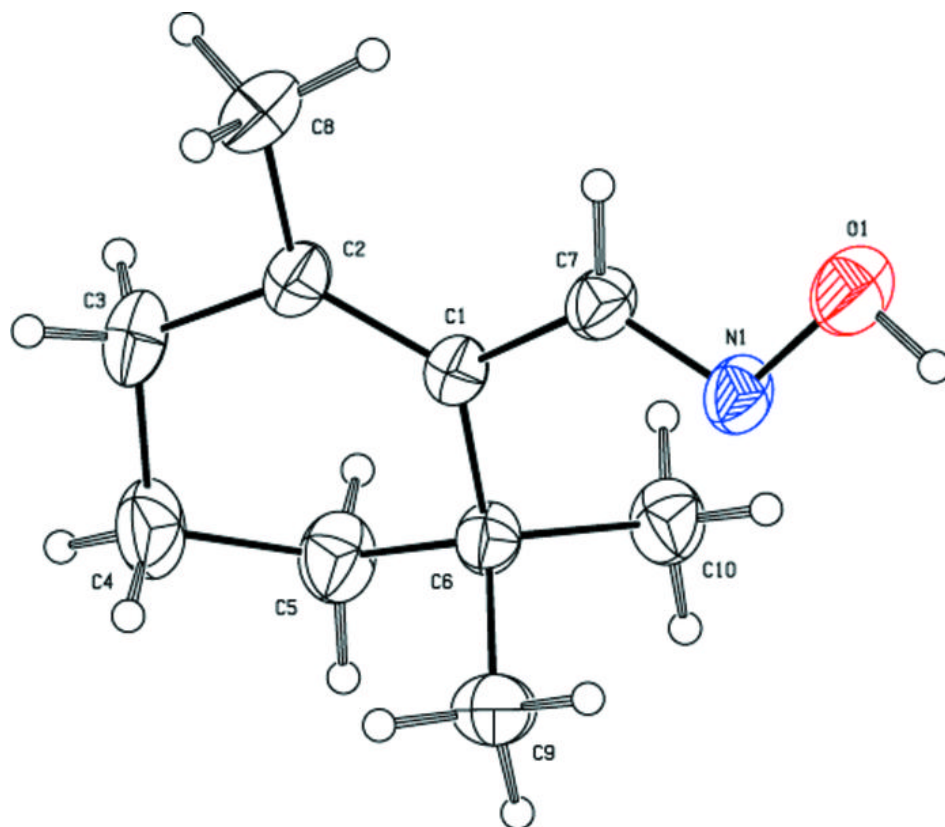




Fig. 2

